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NITRATES IN CAVE EARTHS

A NEW theory of the origin of nitrates in cave earths has been recently propounded by Mr. William H. Hess (JOUR. GEOL., Vol. VII, p. 2) who considers that they are the product of the nitrifying bacteria in the soil above, and that they enter the cave with the seepage through the roof and are deposited by the total evaporation of the water in the dryer parts of the cave. In other words the dry galleries and chambers of a cave serve as a gigantic natural still, catching the seepage from the surface and retaining the solids. Inasmuch as the older theory that these nitrates are leached from the bat guanos formed in the caves is on the face of it sufficient to account for the facts while difficulties arise in the application of the new theory a comparison would seem to be in order. The first and most serious objection Mr. Hess urges against the older theory is a statement that bats never go far from the mouth of the cave, while many analyses (not quoted) show that the nitrates are distributed through the dry chambers of the cave. This would seem to be decisive if rigorously verified, for if bats never went far from the entrance it would be exceedingly difficult to account for the presence of derivatives of bat guano in all dry portions of the cave. In reality, bats frequent in very large numbers remote portions of caves. Dr. O. C. Farrington, in a recent expedition through the caves of Indiana, found bats in all parts of the caves visited.¹ Mr. Hess' second objection is that the cave earth contains little or no organic matter. Two specimens in the collections of the Field Columbian Museum, one from Indiana and one from South America do contain organic matter visible on casual inspection. As the niter, according to the general opinion, is for the most part not a decomposed or altered guano but a residual clay or sand impregnated with soluble salts by seepage from bat guano, there is no reason why it should

¹Field Columbian Museum Publication 53, p. 244.

contain insoluble organic matter or more organic matter than is indicated by the amount of nitrogen and chlorine shown by Mr. Hess' analyses. This objection, apparently based on inspection of the specimens and a single analysis, cannot therefore be considered proven. The third objection made by Mr. Hess to the origin of nitrates in the cavern itself is that while the cave earth and the bat guano contain approximately equal quantities of phosphates, the soluble phosphate is much less in the underlying earth than in the overlying guano. This, however, is merely an illustration of a phenomenon with which all phosphate manufacturers are familiar, viz., the "reversion" of the soluble to the insoluble phosphate by virtue of which a very large percentage of the "available" or soluble acid calcium phosphate of a "superphosphate" when applied to the soil, changes to various insoluble phosphates.¹ It does not appear, then, that any of the above objections are in any sense conclusive.

In support of the external origin of the nitrates, Mr. Hess calls attention to the fact that the leachings from the surface subsoil contain nitrates in small quantity. He also attempts to show by analyses that the soluble portions of the niter earth might be the concentration of the leachings from surface soils, although the figures he gives appear to prove the reverse. Inasmuch as both the niter earth and the surface soil are both (in the Kentucky and Indiana caves) residual soils from limestone, contaminated with organic matter, a general similarity in consequence of similarity of origin is to be expected and is found. But if the soluble salts of the niter earths are the soluble salts transported from the overlying soil, more than a general resemblance should appear. After due allowance is made for compounds which will not redissolve the two should be practically identical if the analyses correctly represent the average constitution of the mixtures in question. As printed, Mr. Hess' analyses do not admit of ready comparison. If the analysis which he gives (p. 131) of subsoil over Mammoth Cave and of the cave earth directly below are recalculated so as

¹ WYATT: Phosphates of America.

to indicate the percentage composition of the soluble portion (on the assumption that the analyses are complete) they compare as follows:

SALTS LEACHED FROM SUBSOIL AND FROM CAVE EARTH, MAMMOTH CAVE

	Na ₂ O+K ₂ O	CaO	SO ₃	P ₂ O ₅	N ₂ O ₅	NH ₄
1. Subsoil.	15.32	9.58	28.72	tr.	36.17	10.21
2. Cave earth.....	28.94	20.54	42.10	0.003	8.30	00.001

The resemblance is purely qualitative, and it is very evident that the second substance could not be formed by the evaporation of a solution of the first as the theory requires. The water which enters the cave forms stalactites and stalagmites and, therefore, must carry carbonate of lime. In the aqueous extract from the subsoil, considered below, the bases are saturated with nitric and sulphuric acid and hence it contains no carbonates. This analysis therefore does not represent the waters which enter the cave. It is most probable that these waters after leaving the subsoil take up carbonate of lime and other material while passing through the rock roof and enter the cave with the composition of the drip water whose analysis is given by Mr. Hess (*loc. cit.*, p. 132).

From the analysis of waters dripping into Mammoth Cave made by Mr. Hess, the figures below have been derived calculating the ratio of certain salts for comparison with the soluble salts from the cave earths of Mammoth and Saltpeter Caves, also recalculated from Mr. Hess' analyses.

SALTS LEACHED FROM CAVE EARTH COMPARED WITH CORRESPONDING SALTS FROM DRIP WATER

	K ₂ O+Na ₂ O	CaO	SO ₃	P ₂ O ₅	Cl	N ₂ O ₅	NH ₄
Certain salts from drip water,							
Mammoth Cave.....	23.24	42.37	22.18	tr.	3.83	8.06	0.06
Cave earth, Mammoth Cave..	27.23	19.91	40.56	5.26	6.95	0.09
" " "	22.39	23.56	33.65	10.38	10.01	0.007
" " Saltpeter Cave...	22.62	23.13	33.03	2.30	18.82	0.07

From this table it is evident that solids from the drip water contain practically twice as much lime as those from the cave earth and much less sulphates and chlorides. Exact calculations for the saturation of bases by alkalies cannot be made without knowing the ratio of soda to potash. An inspection of similar determinations for many Kentucky soils shows for similar situations a ratio of potash to soda of 1 : 4. Assuming this ratio, then, in the case of the drip water, after all the acids are saturated there is a large excess of lime left. This holds true both for the salts given in the above table and for the full analysis as given by Mr. Hess. This lime is held as carbonate and would be deposited as calcite upon evaporation. But in the salts extracted from the cave earths, as before noted, we find that the acids nearly saturate the bases and there is little lime left as carbonate. While the quantities will change as we assume more or less soda in the mixed alkalies, yet the proportions do not vary to any important degree, and in any conceivable case there is a very large excess of calcite in the drip water unaccounted for in the cave earth. In short, the drip in Mammoth Cave carries chiefly carbonates, while the cave earths carry chiefly sulphates. For the drip water to deposit any nitrate it is necessary that it should evaporate practically to dryness and deposit essentially all of its lime and other salts. For every 8 parts of nitric acid, 42 parts of lime will be deposited, and thus the deposit would take the form of stalagmite enclosing the clay or sand, a form of deposit actually found in places but not forming any portion of the cave earth.

The removal of nitrates from guano to cave earth is different. The drip becomes saturated with salts while passing through the guano, deposits only part of its burden in the underlying cave earth, and drains off with the remainder. The deposits thus formed will be composed chiefly of the more soluble instead of the less soluble salts, and no stalagmite will form. This may be made more evident by assuming an ideal case. Take 1 liter of water saturated with calcium nitrate, calcium carbonate, and carbonic acid at 54° F. Keeping the temperature constant, let

the water evaporate until only $\frac{3}{4}$ liter remains. One liter of water at 54° F. will hold in solution approximately 1100 grams of calcium nitrate¹ and (disregarding the influence of the calcium nitrate) only 0.88 gram of calcium carbonate.² When reduced to $\frac{3}{4}$ liter by evaporation it will hold only 825 grams of calcium nitrate and 0.66 gram of calcium carbonate. If the solution be now removed, there remains a precipitate of 275 grams of calcium nitrate and only 0.22 gram of calcium carbonate. This applies to all cases of soluble with slightly soluble salts except where chemical actions intervene, as in the case of phosphates. In one specimen from Dixon's Cave the analysis of the cave earth, recalculated below, shows a very large excess of carbonates. In this case the amount of soluble salts is very minute (0.5655 per cent.), and we probably have the beginning of a stalagmite deposit forming in the nitrates. Over 90 per cent. are bases, with only $5\frac{1}{2}$ per cent. of sulphuric acid. There is no analysis of dropping waters for comparison in this case, however.

SALTS LEACHED FROM CAVE EARTH AND OVERLYING BAT GUANO,
DIXON'S CAVE.

	NaO ₂ + KO	CaO	SO ₃	P ₂ O ₅	Cl	N ₂ O ₅	NH ₄
1. Bat guano, Dixon's Cave.	3.50	31.68	6.35	0.42	—	57.08	0.97
2. Cave earth underlying 1	45.98	40.67	5.48	2.42	—	2.09	3.36

As the overlying bat guano in this case yields up to water salts of which over 57 per cent. are nitric acid, it is difficult to understand how a water carrying the traces of nitrates from the surface of the earth could penetrate this guano to the underlying cave soil without taking along much more nitric acid from the bat guano than the almost infinitesimal quantities it brings from the surface. In this case the soluble part of the deposit is undoubtedly a mixture of the matter in the drip and the matter leached from the bat guano, and there is a bare possibility that

¹ OSTWALD: Outlines of Theoretical Chemistry, p. 150.

² ROSCOE and SCHORLEMMER: Treatise on Chemistry, Vol. II, Pt. I, p. 209.

a very small quantity of nitrate from the surface may be mixed with the much larger quantity leached from the bat guano above.

There are, however, better indicators than the carbonate or sulphate of lime. These are chlorine and the phosphates. The chlorine has not been given in a sufficient number of Mr. Hess' analyses to be available in this discussion, but the data regarding the phosphates are more complete. Inasmuch as phosphates "revert" or become insoluble, the total phosphate, not the soluble, must be considered. Mr. Hess finds only traces of phosphate in the drip or in the soluble extract from the soils of the surface, while the quantity of phosphoric acid in the guano and the niter earth is approximately equal and is very considerable, 2.62 per cent. and 2.10 per cent. respectively. While the approximation to equivalence is doubtless accidental, yet it is undeniable that there is in cave earth much more phosphate in proportion to the niter, alkalies, etc., than the drip water could bring in. An abundance of phosphate is found in soluble form in the bat guano. Mr. Hess regards this excess of phosphate as a concentration in the residual soil, of the calcium phosphate of the limestone on account of its insolubility. But it appears from the figures given by Penrose and others¹ that the percentage of phosphate of lime in limestone and in its residual clay is approximately the same, the larger part of the phosphate going into solution with the carbonate of lime. Penrose selected clay from a hollow in the limestone where it was overlain by 15 feet of similar clay and a chert cap, and compared it with the limestone. He found phosphoric acid in the limestone 3.02 per cent. and in the clay 2.53 per cent. It is not contended that under exceptional circumstances phosphates may not be concentrated as a residuum after solution of limestone, as Safford claims for those of Tennessee, but it is contended that such concentration, if it occur at all, is very unusual, and furthermore that it does not occur in the cave regions of Kentucky and Indiana.

Although no determinations of phosphoric acid in limestone and its residual soil can be found for the immediate vicinity of

¹ MERRILL: *Rocks, Rock Weathering, and Soils*, p. 232.

Mammoth and the other caves considered, yet the above conclusion may be confirmed for the State of Kentucky by the following figures from the analyses of rock and soil made for the Kentucky Geological Survey.¹

No.	Substance.								P ₂ O ₅ , per cent.
570.	Subsoil	-	-	-	-	-	-	-	0.440
571.	Red underclay	-	-	-	-	-	-	-	0.425
572.	Limestone	-	-	-	-	-	-	-	0.221
573.	Limestone	-	-	-	-	-	-	-	0.196
576.	Subsoil, Bourbon county	-	-	-	-	-	-	-	0.243
577.	Underclay	-	-	-	-	-	-	-	0.221
578.	Limestone	-	-	-	-	-	-	-	0.093
579.	Limestone	-	-	-	-	-	-	-	0.183
614.	Subsoil	-	-	-	-	-	-	-	0.316
615.	Limestone	-	-	-	-	-	-	-	0.311
663.	Virgin soil, Jessamine county	-	-	-	-	-	-	-	0.239
664.	Virgin soil, Jessamine county	-	-	-	-	-	-	-	0.666
666.	Limestone	-	-	-	-	-	-	-	0.567
683.	Subsoil	-	-	-	-	-	-	-	0.459
684.	Underclay	-	-	-	-	-	-	-	0.456
685.	Limestone	-	-	-	-	-	-	-	0.631

In preparing the above table all cultivated soils have been excluded, and it is believed that only examples of virgin soils, subsoils and underlying limestones that are properly comparable have been included. The average of these figures is 0.315 per cent. P₂O₅ for the limestones and 0.365 per cent. P₂O₅ for the soils. The average of twenty-five analyses of subsoils overlying limestone in Kentucky is 0.264 per cent. P₂O₅. Mr. Hess finds 2.62 per cent. P₂O₅ in bat guano and 2.10 per cent. P₂O₅ in cave earth. This is obviously a far greater proportion of phosphate than is found in other residual clays, and as in the drip water he finds only a trace of phosphate with 53.61 milligrams carbonate of lime, the difference can hardly be made up from that source. On the other hand, the bat guano provides an abundant supply, as all the phosphorus used in the metabolic processes of bat life must eventually find its way to the guano. Finally, it

¹ Third Report Geol. Surv. Kentucky.

may be noted that Mr. Hess' claim that nitrates are uniformly distributed in the dry chambers of caves is not substantiated by the analyses of cave earths of Wyandotte Cave made for the Indiana Geological Survey.¹ Besides the analysis of niter earth, there is given one of the magnesian earth which is abundant in the dry portions of Wyandotte Cave. The analysis of this earth shows no nitrates. An interesting variation between the distribution of nitrates and of other nitrogen compounds throws much light upon the problem, and has been investigated by Müntz and Maracano for some Venezuelan caves.² "There is thus a gradual change in the character of the nitrogenous combination from the interior to the exterior portions of the cave, as shown in the following analyses:

Constituents	Guano from interior of cave	Earth from entrance	Earth some distance from entrance
Organic nitrogen	11.74 per cent.	2.41 per cent.	0.80 per cent.
Nitrate of lime	0.00 "	3.03 "	10.36 " "

If the transformation of organic nitrogen through ammonia and nitrites to nitrates by the action of bacteria occurs only at the surface, there should be no uniform variation in the proportions of these components in the cave earths, but such a variation as has been found might occur from the mouth of the cave inward if the bacteria are acting in the cave itself. Mr. Hess has doubtless performed a service in pointing out a method by which cavern deposits of nitrates may be formed, and it is not improbable that such deposits may be discovered. Deposits thus formed, however, will have several easily recognized features not found in the cavern earths now known.

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FIELD COLUMBIAN MUSEUM,
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¹ Indiana Geol. Surv., 1878, p. 162.

² MERRILL: Rocks, Rock Weathering, and Soils, p. 372.